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(54) Title: RADIATION CURABLE COMPOSITIONS BASED ON UNSATURATED POLYESTER, VINYL ETHER AND URETHANE VINYL ETHER COMPOUNDS

(57) Abstract

Disclosed is a radiation curable composition which includes: (a) an unsaturated polyester compound, (b) a polymerizable vinyl ether compound, and (c) a polymerizable urethane vinyl ether compound. The unsaturated polyester compound is characterized as having more than 2.0 unsaturated ester groups per molecule and being the reaction product of unsaturated carboxylic acids and/or blends of unsaturated and saturated carboxylic acids with polyhydric alcohols and/or blends of polyhydric and monohydric alcohols. The polymerizable vinyl ether compound is characterized as including at least one of the following: (a) a compound having an average of greater than 1.0 reactive vinyl ether groups per molecule, and (b) a vinyl ether–containing group bonded to the unsaturated polyester compound such that there is an average of at least 1.0 reactive vinyl ether group per molecule. The polymerizable urethane vinyl ether compound is characterized as having a saturated urethane–containing backbone with vinyl ether groups. The polymerizable vinyl ether and urethane vinyl ether compounds are able to react, upon exposure to radiation, with the ethylenic unsaturation of the unsaturated polyester compound.

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RADIATION CURABLE COMPOSITIONS BASED ON UNSATURATED POLYESTER, VINYL ETHER AND URETHANE VINYL ETHER COMPOUNDS

BACKGROUND OF THE INVENTION

The technical field of the present invention relates to radiation curable compositions. Particularly, it relates to radiation curable coating compositions containing unsaturated polyester compounds in combination with vinyl ether compounds.

There are a number of coating applications requiring the use of coating compositions that cure rapidly, adhere well to a substrate and do not discolor during the curing process. In some instances, radiation curable coating compositions can be used to meet these objectives.

The basic chemistry of radiation curing involves a rapid polymerization of unsaturated materials initiated by free radicals formed when the system is irradiated by ionizing radiation and/or actinic radiation, hereinafter individually and collectively referred to as "radiation." One of the major components of many conventional radiation curable coating compositions are acrylates or methacrylates (hereinafter individually and collectively referred to as "(meth)acrylates").

Notwithstanding the widespread use of radiation curable coating compositions which include (meth)acrylates as one of their major components, there are problems associated therewith. For example, their cure response is significantly inhibited by the presence of oxygen in the curing atmosphere. Moreover, there are also concerns with the possibility of skin and eye irritation sometimes associated with their the used and/or handling. For these and other reasons, it is becoming desirable in the coating industry to reduce and/or eliminate the amount of (meth)acrylates present in radiation curable coating compositions.

One alternative to such conventional radiation curable coating compositions is disclosed in commonly-owned U.S. Patent No. 5,536,760. Specifically, that patent discloses radiation curable coating compositions having, as their major components, ethylenically unsaturated ester compounds having a plurality of

unsaturated ester groups and polymerizable vinyl ether compounds. In one preferred embodiment of that patent, the unsaturated ester compounds are polyunsaturated polyesters having more than 2.0 unsaturated ester groups per molecule.

Coatings produced in accordance with U.S. Patent No. 5,536,760 have a relatively fast cure response when exposed to radiation. If a large number of ethylenically unsaturated groups are present in the unsaturated ester compounds, the coatings disclosed therein have the potential of being hard and brittle. Although there are many applications where properties such as hardness and brittleness are highly desirable, it is sometimes equally desirable for radiation-cured coating composition to be hard and flexible. Moreover, notwithstanding their relatively fast cure response, it is also often desirable to even further accelerate the cure rates of such coating compositions.

U.S. Patent Nos. 5,334,455; 5,334,456 and 5,340,653, all having the same inventive entity, disclose radiation curable coating compositions having two major components. The first major component for all three patents is a compound containing at least one vinyl ether group. According to all of these patents, preferred vinyl ether-containing compounds have the formula:

$$R^3 - (O - CH = CHR^4)_m$$

where:

m is an integer from 1 to 5;

R^3 is a residue of an organic alcohol or polyol, substantially free of maleate or fumarate groups, with a molecular weight from 56 to 2,000; and

R^4 is hydrogen or methyl.

These patents also disclose that the vinyl ether-containing first component can be produced by conventionally reacting a vinyl ether having either a hydroxyl group or amine group with a saturated backbone containing component. This saturated backbone containing component may be the reaction product of saturated hydroxy functional polyesters, polycarbonates, polycaprolactones, polyethers, bisphenol A alkoxylates or siloxanes with organic polyisocyanates. The group linking the vinyl ether group to the

saturated backbone in these patents can be a urethane, urea, ester, ether or thio group. These patents further disclose that the vinyl ether-containing first component can be polyvinyl ether polyurethanes and saturated polyesters.

The second component of U.S. Patent No. 5,334,455 is a compound having epoxy-containing backbones and maleate and/or fumarate end groups. The second component of U.S. Patent No. 5,334,456 is a compound having saturated polyester backbones and maleate and/or fumarate end groups. The second component of U.S. Patent No. 5,340,653 is a compound having urethane backbones and maleate and/or fumarate end groups. The second component each of these patents must be capped with maleate and/or fumarate groups. According to each of these patents, the resulting cured coatings exhibit good flexibility, tensile strength, percent elongation and good adhesion to substrates. In U.S. Patent No. 5,334,455 these desired properties are due to the presence of the epoxy backbones in the compound having maleate and/or fumarate end groups; in U.S. Patent No. 5,334,456, these desired properties are due to the presence of the saturated polyester backbones in the compound having maleate and/or fumarate end groups; and in U.S. Patent No. 5,340,653, these desired properties are due to the presence of the urethane backbones in the compound having maleate and/or fumarate end groups. Each of these patents further recite that the prior art radiation curable coatings produced from materials having maleate and/or fumarate unsaturated backbones tend to be hard and brittle.

U.S. Patent No. 5,200,490 discloses radiation curable coating compositions which contain polyurethane vinyl ethers. Such polyurethane vinyl ethers are obtained by reacting: (a) 1 NCO equivalent of 1 or more isocyanurate-containing polyisocyanates with (b) 0.01 to 1.0 equivalent of one or more monohydroxy vinyl ethers, and (c) 0 to 0.99 equivalent of functional groups of further compounds which react with NCO groups to saturate isocyanate groups which have not reacted with monohydroxy vinyl ethers so that no free isocyanate is present in the resulting polyurethane vinyl ethers. The isocyanurate-containing compounds disclosed therein are cationically cured, as opposed to free radically cured. Cationic cure systems are sometimes less desirable than free radical cure systems due to the former's moisture sensitivity of the resulting cured coating.

SUMMARY OF THE INVENTION

One object of the present invention is to provide hard and flexible radiation curable coating compositions which do not require the use of (meth)acrylates as one of their major components.

Another object of the present invention is to provide radiation curable coating compositions having an improved cure response.

Still another object of the present invention is to provide radiation curable coating compositions with improved oxygen tolerance during the curing process.

Yet another object of the present invention is to provide substrates having cured thereon at least one film comprising the radiation curable coating compositions of the present invention.

These and other objects are achieved by the advent of novel, radiation curable coating compositions which include: **(a)** an unsaturated polyester compound; **(b)** a polymerizable vinyl ether compound ; and **(c)** a polymerizable urethane vinyl ether compound having a saturated, urethane-containing backbone with vinyl ether groups.

The present invention also provides substrates having cured thereon a film of radiation curable coating compositions described above.

DETAILED DESCRIPTION OF THE INVENTION

The term "unsaturated polyester compound" as used herein refers to a polyunsaturated polymer(s) and/or an oligomer(s) having more than 2.0 unsaturated ester groups per molecule and being prepared by the reaction of unsaturated carboxylic acids and/or blends of unsaturated and saturated carboxylic acids with polyhydric alcohols and/or blends of polyhydric and monohydric alcohols.

The terms "polymerizable vinyl ether compound" and "polymerizable urethane vinyl ether compound" as used herein refer to compounds having vinyl ether groups which can react, upon exposure to radiation, with the ethylenic unsaturation of the unsaturated polyester compound.

The unsaturated polyester compound which can be used when practicing this invention includes hydroxy functional unsaturated polycarboxylates, polycaprolactones, and the like. In a preferred embodiment, the unsaturated polyester compound is a hydroxy functional unsaturated polycarboxylate which is the esterification product of an ethylenically unsaturated carboxylic acid and a polyhydric alcohol.

Unsaturated carboxylic acids which can be used in preparing such a preferred unsaturated polyester compound include unsaturated carboxylic acids having an acid functionality of at least two and/or their corresponding anhydrides. Examples of such unsaturated carboxylic acids and/or their anhydrides which can be used for this purpose include: maleic acid, maleic anhydride, fumaric acid and itaconic acid.

Since it is readily available and relatively inexpensive, maleic anhydride is economically desirable. However, since maleate esters do not copolymerize with vinyl ethers as readily as fumarate esters (*e.g.*, esters derived from fumaric acid), fumarate esters are preferred for making the unsaturated ester compound of the present invention when increased cure response is an objective.

The unsaturated carboxylic acids used in preparing the aforementioned preferred unsaturated polyester compound can also be blended with a saturated carboxylic acid. Examples of saturated carboxylic acids which can be used for this purpose include: phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, adipic acid, azelaic acid, sebacic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, suberic acid, 2,2-dimethylsuccinic acid, 3,3-dimethylglutaric acid, 2,2-dimethylglutaric acid and mixtures thereof. Moreover, anhydrides of the saturated carboxylic acids, where they exist, can also be used for this purpose.

Polyhydric alcohols which can be used in preparing the aforementioned preferred unsaturated polyester compound include: diethylene glycol, ethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexane-dimethanol, 1,2-bis(hydroxyethyl)cyclohexane, and 2,2-dimethyl-3-hydroxypropyl-2,2-

dimethyl-3-hydroxypropionate, neopentyl glycol, 2-methyl-1,3-propane diol and the like and/or mixtures thereof.

Preferably, the polyhydric alcohols which are used in preparing the aforementioned preferred unsaturated polyester compound are diols. Specifically, while polyols having a hydroxyl functionality greater than two may be used for this purpose, it is preferred that the major portion, if not all, of the unsaturated polyester compounds used in this invention be comprised of linear, unsaturated polyester molecules. Since it is readily available and relatively inexpensive, diethylene glycol is a particularly preferred diol which can be used for this purpose.

The polyhydric alcohols used in preparing the aforementioned preferred unsaturated polyester compound can also be blended with monohydric alcohols. Examples of monohydric alcohols that can be used for this purpose include C_1 to C_{15} alcohols.

The molecular weight of the unsaturated polyester compound employed when practicing this invention can vary widely. However, as measured by gel permeation chromatography (hereinafter "GPC") using a polystyrene standard, the unsaturated polyester compound typically has a peak molecular weight ranging from about 500 to about 50,000; preferably from about 600 to about 25,000; more preferable from about 700 to about 10,000; and even more preferably from about 800 to about 5,000.

The unsaturated polyester compound can be prepared by a number of different procedures known to those skilled in the art. In one preferred embodiment, the unsaturated polyester compound is prepared by heating a mixture of an unsaturated carboxylic acid or a blend of unsaturated and saturated carboxylic acids with a polyhydric alcohol or a blend of monohydric and polyhydric alcohols for about 1 to about 10 hours at temperatures ranging from about 150° C. to about 250° C, with water formed during the esterification being distilled off using a sparge of an inert gas such as nitrogen. Esterification catalysts, which increase the rate of such a reaction, can also be used in this process. Examples of suitable esterification catalysts include: para-toluenesulfonic acid, butylstannoic acid, dibutyltin oxide, stannous fluoride and stannous octoate.

The coating compositions prepared in accordance with this invention also include a polymerizable vinyl ether compound. The polymerizable vinyl ether compounds of this invention can react with the unsaturated polyester compounds and include: **(a)** compounds which have an average of greater than 1.0 reactive vinyl ether groups per molecule and/or **(b)** a vinyl ether-containing group bonded to an unsaturated polyester compound such that the resulting compound has an average of at least 1.0 reactive vinyl ether group per molecule. The vinyl ether groups of the polymerizable vinyl ether compound are different from, and cocurable with, the ethylenically unsaturated moieties in the backbone of the unsaturated polyester compound(*e.g.*, those provided from the residue of the unsaturated carboxylic acid used in making an unsaturated polyester polymer and/or oligomer).

Examples of compounds containing greater than 1.0 reactive vinyl ether groups per molecule include vinyl ethers made in known manners from di-, tri-, or tetrafunctional polyols, acetylene and a basic catalyst under pressure. It also includes vinyl ether terminated polyesters such as those made in accordance with the processes disclosed in U.S. Patent No. 5,286,835. Specific examples of such compounds include: tripropylene glycol divinyl ether, diethylene glycol divinyl ether, 1,4-butanediol divinyl ether, tetraethylene glycol divinyl ether, triethylene glycol divinyl ether, trimethylolpropane trivinyl ether, polytetrahydrofuran divinyl ether, vinyl ether terminated polyesters and the like, and combinations thereof. Triethylene glycol divinyl ether is the preferred vinyl ether compound for use in this invention.

One example of a compound having at least 1.0 reactive vinyl ether-containing group bonded to the unsaturated polyester compound which can be used when practicing this invention can be made by polymerizing a hydroxy-functional vinyl ether (*e.g.*, hydroxybutyl vinyl ether) with a polyisocyanate (*e.g.*, isophorone diisocyanate) to form a half-capped isocyanate adduct. Thereafter, residual isocyanato functionality of the half-capped adduct is reacted with the hydroxyl functionality of an unsaturated polyol so as to structurally incorporate of at least 1.0 reactive vinyl ether groups in the unsaturated polyester compound. Examples of unsaturated carboxylic acids, unsaturated carboxylic acid anhydrides and polyols which are suitable for preparing such hydroxyl-functional unsaturated polyester resins include those described herein

previously. Examples of polyisocyanates which can be used for this purpose include: toluene-2,4-diisocyanate, toluene-2,6-diisocyanate; diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate; para-phenylene diisocyanate; biphenyl diisocyanate; 3,3'-dimethyl-4,4'-diphenylene diisocyanate; tetramethylene-1,4-diisocyanate; hexamethylene-1,6-diisocyanate; 2,2,4-trimethylhexane-1,6-diisocyanate; lysine methyl ester diisocyanate; bis(isocyanatoethyl)fumarate; isophorone diisocyanate; ethylene diisocyanate; dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate; methylcyclohexyl diisocyanate; hexahydrotoluene-2,4-diisocyanate, hexahydrotoluene-2,6-diisocyanate; hexahydrophenylene-1,3-diisocyanate, hexahydrophenylene-1,4-diisocyanate; perhydrodiphenylmethane-2,4'-diisocyanate, perhydrodiphenyl-methane-4,4'-diisocyanate, 4,4'-methylene-bis-(cyclohexyl isocyanate) and the like, and/or mixtures thereof. The resulting unsaturated polyester compounds contain urethane moieties and are usually free of unreacted isocyanate groups.

The vinyl ether compound used when practicing this invention can also include a blend of a compound having an average of greater than 1.0 reactive vinyl ether groups per molecule and a compound having at least 1.0 reactive vinyl ether-containing groups bonded to the unsaturated polyester compound. Examples of both such vinyl ether-containing compounds include those previously described herein.

The coating compositions prepared in accordance with this invention also include a polymerizable urethane vinyl ether compound. The polymerizable urethane vinyl ether compound of this invention can also react with the unsaturated polyester compound. This urethane vinyl ether compound has a saturated, urethane-containing backbone with vinyl ether groups linked thereto.

The urethane vinyl ether compound used when practicing this invention can be produced conventionally by reacting a vinyl ether compound having hydroxyl group and/or amine group functionality with a compound having a saturated, urethane-containing backbone and isocyanate functionality. For urethane vinyl ether compounds prepared in such a conventional manner, the compound having the saturated, urethane-containing backbone is typically made by the polymerizing polyisocyanates with saturated, hydroxy-functional compounds. Examples of saturated, hydroxy-functional

compounds which can be used for this purpose include: polyesters, polycarbonates, polycaprolactones, polyethers, bisphenol A alkoxylates and siloxanes.

In one preferred embodiment for making the urethane vinyl ether compound used when practicing this invention, the saturated, hydroxy-functional compound comprises a saturated polyester which includes soluble reaction products of saturated polycarboxylic acids (or their anhydrides) with polyols. Examples of suitable saturated polycarboxylic acids and anhydrides which can be used for this purpose include: phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, adipic acid, azelaic acid, sebacic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, suberic acid, 2,2-dimethyl succinic acid, 3,3-dimethylglutaric acid, 2,2-dimethyl glutaric acid, anhydrides thereof and/or mixtures thereof. Moreover, examples of polyols that can be used for this purpose include: diethylene glycol, ethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexane-dimethanol, 1,2-bis(hydroxyethyl)cyclohexane, and 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, neopentyl glycol, 2-methyl-1,3-propane diol and the like and/or mixtures thereof.

The vinyl ether compounds which react with the aforementioned compounds having a saturated urethane-containing backbone have hydroxyl group and/or amine group functionality. Preferably, such vinyl ether compounds have hydroxyl group functionality. Examples of hydroxy-functional vinyl ether compounds which can be used for this purpose include: triethylene glycol monovinyl ether; 1,4-cyclohexane dimethylol monovinyl ether, 1-methyl-3-hydroxypropyl vinyl ether, 4-hydroxybutyl vinyl ether and mixtures thereof. For processing and commercial reasons, the preferred hydroxy-functional vinyl ether compound used to produce the urethane vinyl ether compounds of this invention is 4-hydroxybutyl vinyl ether.

In the urethane vinyl ether compound, the groups linking the vinyl ether groups to the saturated, urethane-containing backbone component is typically at least one of the following: urethane, urea, ester, ether and thio groups. Examples of

preferred linking groups include urethane, urea and/or ester groups. More preferably, the linking groups are urethanes.

Urethane vinyl ether compounds can also be prepared by polymerizing a hydroxy-functional vinyl ether (*e.g.*, hydroxybutyl vinyl ether) with a polyisocyanate (*e.g.*, isophorone diisocyanate) to form a half-capped diisocyanate adduct. Thereafter, residual isocyanato functionality of the half-capped adduct is reacted with the hydroxyl functionality of a saturated polyol so as to structurally incorporate an average of at least 1.0 reactive vinyl ether groups per molecule.

The molecular weight of the urethane vinyl ether compound used when practicing this invention can vary widely. Typically, it has a peak molecular weight, as measured by GPC using a polystyrene standard, ranging from about 200 to about 50,000; preferably from about 300 to about 25,000; more preferably from about 400 to about 15,000; and even more preferably from about 500 to about 5,000.

In the radiation curable coating compositions of the present invention, the ratio of the sum of the carbon-carbon double bond equivalents from the vinyl ether and urethane vinyl ether compound to the carbon-carbon double bond equivalents from the unsaturated polyester compound typically ranges from about 0.1:1 to about 1.5:1; preferably from about 0.2:1 to about 1.4:1; and more preferably from about 0.3:1 to about 1.2:1. However, for many coating purposes, it is often desirable that the aforesaid ratio of carbon-carbon double bond equivalents be approximately 1:1.

Of the total carbon-carbon double bond equivalents provided by the vinyl ether and urethane vinyl ether compound, that portion derived solely from the urethane vinyl ether compound typically ranges from about 1 % to about 99 %; preferably from about 3 % to about 85 %; more preferably from about 5 % to about 65%; and even more preferably from about 10 % to about 50 %.

The vinyl ether, urethane vinyl ether and unsaturated polyester compounds are employed in the radiation curable composition of the present invention in relative amounts to obtain the desired ratio of carbon-carbon double bond equivalents so as to provide crosslinking via reaction of ethylenic unsaturation provided from the unsaturated polyester compound with vinyl unsaturation provided by the vinyl ether and

urethane vinyl ether compound upon free-radical curing of the composition (*e.g.*, when exposed to radiation).

The radiation curable coating composition of the present invention are essentially free of components that would destabilize the coating composition during processing, handling and/or application procedures by initiating the premature polymerization of the vinyl ether and/or urethane vinyl ether compounds (hereinafter referred to as "destabilizing agents"). Examples of a components that would destabilize the coating compositions prepared in accordance with this invention is oxidizing agents. Specifically, the presence of a sufficient amount of destabilizing agents (*e.g.*, peroxides and hydroperoxides) in the unsaturated polyester, vinyl ether and/or urethane vinyl ether compounds may initiate polymerization prior to their being blended together and exposed to radiation. Moreover, even if the vinyl ether and/or urethane vinyl ether compound is/are essentially free of destabilizing agents, the presence of destabilizing agents in the unsaturated polyester compound may still cause premature polymerization when all of the components are mixed together.

Under properly controlled conditions, it is possible to prepare the unsaturated polyester, vinyl ether and urethane vinyl ether compounds in a manner such that they are all essentially free of destabilizing agents. It is also possible to handle these compounds and/or any mixture thereof in a manner such that they remain essentially free of destabilizing agents until polymerization is initiated by exposure to radiation. However, in those instances where the processing and/or handling conditions are such that it is difficult to keep the compounds and/or mixtures thereof essentially free of destabilizing agents prior to their exposure to radiation, it is preferred to blend these compounds with a reducing agent so as to decompose at least some of the destabilizing agents which are, or may be, present therein.

Reducing agents which can be used to stabilize the radiation curable coating compositions prepared in accordance with this invention are those which, while being able to decompose destabilizing agents do not adversely affect the properties of the compounds which they are blended and/or the resulting radiation curable coating composition. Examples of such reducing agents include organic phosphites such as: dimethyl-phosphite, dioctyl-phosphite, diphenyl-phosphite, tri-octyl-phosphite, tri-

stearyl-phosphite, trimethyl-phosphite, tri-ethyl-phosphite, tri-isopropyl-phosphite, tris-allyl-phosphite, didecyl-phenyl-phosphite, tri-phenyl-phosphite, tris-4-nonylphenyl-phosphite, tris-4-chlorophenyl-phosphite, tri-laurylthio-phosphite, tetraphenyl-dipropylene-glycol-diphosphite and mixtures thereof.

If the mixture of the unsaturated polyester, vinyl ether and urethane vinyl ether compounds is prepared and handled in a manner so as to keep it essentially free of destadilizing agents prior to being exposed to radiation, then it is only necessary to blend reducing agents with those compounds which are not prepared and/or handled in a manner so as to keep them essentially free of destabilizing agents. The amount of a reducing agent necessary to decompose destabilizing agents that are, or may be, present can be added to any one or more of the compounds. However, if all of the reducing agent is added to only some of the compounds, this may not prevent the premature polymerization since the compound(s) to which reducing agents has/have not been added may contain destabilizing agents. Preferably, each of the compounds are individually blended with reducing agents.

The amount of reducing agent employed is that which is necessary to decompose at least some of the destabilizing agents which are, or may be, present in the individual compounds and/or any mixture thereof. Typically, the reducing agent is employed in an amount which is necessary to decompose more than 50% of the destabilizing agents present in the individual compounds and/or any mixture thereof, preferably at least 70%, more preferably at least 90%, and even more preferably, at least 95%.

The amount of reducing agent typically employed is at least about 0.05 weight percent of the respective compound's total resin solids. If two or more of the compounds are blended together prior to being treated with a reducing agent, the amount of reducing agent employed is typically at least about 0.05 weight percent of the blend's total resin solids. Preferably, the amount of reducing agent employed ranges from about 0.05 to about 10 weight percent, more preferably from about 0.1 to about 6 weight percent, and even more preferably from about 0.5 to 3 weight percent. These weight percentages are based upon the respective compound's total resin solids or the blend's total resin solids.

When destabilizing agents are present in the unsaturated polyester, vinyl ether and/or urethane vinyl ether compounds, reducing agents are preferably permitted to react separately with the contaminated compound(s) for a time sufficient to decompose the oxidizing agents present therein. Dwell time for such a treatment process is temperature dependent. For example, sufficient treatment dwell times typically range from about 1 hour at 100° C. to about 24 hours at ambient temperature, preferably from about 2 hours at 100° C. to about 36 hours at ambient temperatures, and more preferably from about 3 hours at 100° C. to about 48 hours at ambient temperatures.

The coating compositions of the present invention can be cured by various conventional means known to those skilled in the art. For example, the coating compositions can be cured by exposure to ionizing radiation (*e.g.*, by electron beam), actinic energy (*e.g.*, by ultraviolet light) and/or thermal energy (*e.g.*, heat). Notwithstanding the above, the preferred method of curing the coating compositions of the present invention is by exposure to radiation (*e.g.*, ionizing and/or actinic radiation).

Ionizing radiation is radiation having energy at least sufficient to produce ions either directly or indirectly in a medium such as air or water. Examples of ionizing radiation sources include accelerated electrons as produced by generally known electron beam devices. When electron beam devices are used to cure coating compositions prepared in accordance with this invention, the energy of the accelerated electrons typically ranges from about 50,000 electron volts to about 300,000 electron volts. The amount of ionizing radiation in rads for curing a composition of the invention will vary depending on factors such as the particular formulation of the radiation curable composition, thickness of the applied layer of coating composition on the substrate, temperature of the composition, and the like.

One advantage of coating compositions prepared in accordance with this invention is their excellent degree of cure at low doses of ionizing radiation. Generally, a 1 mil (25 micron) thick wet film of a coating composition of this invention can be cured in the presence of oxygen through its thickness to a tack-free state upon exposure to from about 0.5 to about 5 megarads of ionizing radiation.

Actinic radiation is light with wavelengths of electromagnetic radiation ranging from the ultraviolet light range, through the visible light range, and into the infrared range. Actinic radiation which can be used to cure coating compositions of this invention generally has wavelengths of electromagnetic radiation ranging from about 150 to about 2,000 nanometers (nm), preferably from about 180 to about 1,000 nm, and more preferably from about 200 to about 500 nm.

Many of the ultraviolet light sources generally known in the art can be used to cure the radiation curable coatings of this invention. Examples of such include: mercury arcs, carbon arcs, low pressure mercury lamps, medium pressure mercury lamps, high pressure mercury lamps, swirl-flow plasma arcs and ultraviolet light emitting diodes. Preferably, ultraviolet light-emitting lamps of the medium pressure mercury vapor type are employed when practicing this invention. Such lamps usually have fused quartz envelopes and are ordinarily in the form of long tubes having an electrode at each end. Preferred medium pressure mercury lamps have outputs ranging from about 200 to about 600 watts per inch (about 79 to about 237 watts per centimeter) across the length of the tube.

Unlike ionizing radiation, actinic radiation does not possess sufficient energy to produce ions in a medium such as air or water. Accordingly, it is necessary to use formulation additives (*e.g.*, photoinitiators and/or photosensitizers) therewith to initiate the polymerization process.

Photoinitiators and/or photosensitizers (individually and collectively referred to hereinafter as "photoinitiators") are typically present in those coating compositions prepared in accordance with this invention which are designed to be cured by actinic radiation since they provide high energy free radicals following radiation. These free radicals, in turn, initiate the polymerization process.

When utilized in the coating compositions of this invention, photoinitiators are typically present an amount ranging from about 0.01 to about 20 weight percent, preferably from about 0.05 to about 15 weight percent, and more preferably from about 0.1 to about 10 weight percent. These weight percentages are based upon the total weight of the coating composition.

Photoinitiators which can be used to cure coating composition prepared in accordance with this invention include those having an absorption in the range from about 150 to about 2,000 nm, preferably from about 180 to about 1,000 nm, and more preferably from about 200 to about 500 nm. When employed in accordance with this invention, the photoinitiators typically comprise at least one of the following compounds: hydroxy- or alkoxy-functional acetophenone derivatives, or benzoyl diaryl phosphine oxides.

Examples of suitable photoinitiators which can be used when practicing this invention include: benzophenone, anthraquinone and thioxanthone, isobutyl benzoin ether, mixtures of butyl isomers of butyl benzoin ether, alpha,alpha-diethoxyacetophenone, alpha,alpha-dimethoxy-alpha-phenylacetophenone, 2-hydroxy-2-methyl-1-phenyl propane 1-one and 2,4,6-trimethyl benzoyl diphenyl phosphine oxide. Other examples of photoinitiators that can be used in the coating compositions of this invention include those set out in U.S. Patent Nos. 4,017,652 and 5,340,653.

Another advantage of coating compositions prepared in accordance with this invention is their excellent degree of cure at relatively low doses of actinic radiation. Generally, a 1 mil (25 micron) thick wet film of a coating composition of this invention which includes a photoinitiator, can be cured through its thickness to a tack-free state upon exposure to actinic radiation by passing the film at a rate of about 20 feet per minute (about 6 meters per minute) or more under four or fewer medium pressure mercury vapor lamps operating at about 200 watts per inch (about 79 watts per centimeter) at a distance of about 4 inches (about 10 centimeters) from the surface of the wet film.

In one preferred embodiment, coating compositions prepared in accordance with this invention additionally contain a light stabilizer. One example of a particularly preferred light stabilizer is bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate. Such a light stabilizer is commercially available from Ciba-Geigy, Inc. as TINUVIN®292 hindered amine light stabilizer.

Optionally, the radiation curable composition of the invention can additionally contain other ethylenically unsaturated monomers or oligomers, examples of which include: vinyl monomers such as vinyl acetate, styrene, vinyl toluene, divinyl benzene, methylvinyl ether, ethylvinyl ether and butylvinyl ether; acrylic and methacrylic esters such as methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, glycerol di(meth)acrylate, glycerol tri(meth)acrylate, 1,3-propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,2,4-butanetriol tri(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,4-cyclohexanediol di(meth)acrylate, 1,4-benzenediol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, 1,5-pentanediol di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, isobornyl (meth)acrylate and tetrahydrofurfuryl (meth)acrylate; (meth)acrylates derived from aromatic glycidyl ethers such as bisphenol A diglycidyl ether and aliphatic glycidyl ethers such as butanediol diglycidyl ether, specific examples of which include 1,4-butanediol diglycidylether di(meth)acrylate, bisphenol A diglycidylether di(meth)acrylate and neopentylglycol diglycidylether di(meth)acrylate; and acrylic or methacrylic amides such as (meth)acrylamide, diacetone (meth)acrylamide, N(beta-hydroxyethyl) (meth)acrylamide, N,N-bis(beta-hydroxyethyl) (meth)acrylamide, methylene bis(meth)acrylamide, 1,6-hexamethylene bis(meth)acrylamide, diethylenetriamine tris(meth)acrylamide, bis(gamma-(meth)acrylamidepropoxy) ethane and beta-(meth)acrylamide ethylacrylate.

Coating compositions of this invention can optionally contain a thermal polymerization inhibitor. Examples of suitable thermal polymerization inhibitors include phenolic compounds such as di-tertiary butyl paracresol and compounds containing secondary or tertiary nitrogen atoms.

Coating compositions of this present invention can optionally contain a solvent component. Examples of solvents which can be used for this purpose include:- conventional aliphatic and aromatic solvents or diluents known in the art.

Coating compositions of this invention can optionally contain a pigment component. When it is desired to cure the composition with actinic radiation, the pigment component typically comprises pigments which do not absorb or block that portion of the light spectrum which is necessary to initiate the photocuring process. Examples of pigments which can be used in the coating compositions of this invention : talc, calcium carbonate, aluminum silicate, magnesium silicate, barytes, titanium dioxide and silica.

Although it is preferred to cure compositions of the present invention by ionizing radiation and/or actinic light, they may be thermally cured in the presence of a thermal free-radical initiator. Examples of thermal initiators suitable for this purpose include: benzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, cyclohexanone peroxide, 2,4-dichlorobenzoyl peroxide, bis(p-bromobenzoyl) peroxide, acetyl peroxide, N,N-azobis(isobutyrylnitrite), metallic dryer systems, redox systems, and the like.

Coating compositions of this invention can be in either a liquid or a solid (*i.e.*, powder) form. These coating compositions can be applied to a variety of substrates, examples of which include: cellulosic materials (*e.g.*, wood, paper, particleboard, chipboard), metals, metals having primers thereon, glass, plastics, metallized plastics, and the like and/or combinations thereof. Moreover, these coating compositions can be applied by a variety of procedures, examples of which include: brushing, dipping, roll coating, doctor blade coating, spraying, curtain coating, and the like and/or combinations thereof.

The examples which follow demonstrate specific embodiments of the present invention and are submitted for the purpose of illustrating features and advantages of coating compositions prepared in accordance therewith.

EXAMPLES

The following examples illustrate the preparation of components of the coating compositions prepared in accordance with this invention, as well as the coating compositions themselves. As used in the examples, all percents, ratios and parts are "by weight," unless otherwise indicated.

EXAMPLE 1

Preparation of an Unsaturated Polyester Compound

This example illustrates the preparation of an unsaturated polyester compound which can be used in radiation curable coating compositions.

A reaction vessel equipped, with means for steam distillation and a nitrogen sparge, was charged, under agitation, with 1527.75 grams diethylene glycol, 259.5 grams butyl carbitol, 666.0 grams neopentyl glycol, 1857.0 grams fumaric acid, 2.08 grams butyl stannoic acid and 0.41 grams methyl hydroquinone. The charge was gradually heated to 250° F. (121° C.) at which time a nitrogen sparge was applied. Heating was continued to a temperature of 410° F. (210° C.) while a total of 564 milliliters of distillate containing water was removed at a head temperature which did not exceed 212° F. (100° C.).

The unsaturated polyester was cooled to 189° F. (87° C.) at which time 11.20 grams dipropylene glycol tetraphenyl diphosphite and 18.7 grams triphenyl phosphite were added thereto. The charge was then held for three hours at about 190° F. (88° C.) The resulting product was an unsaturated polyester resin having an acid value of 4.6 milligrams of KOH/gram of sample, and a Gardner-Holdt bubble tube viscosity of Z4+ at a 100 percent by weight solids.

EXAMPLE 2

Preparation of a Urethane Vinyl Ether Compound

This example illustrates the preparation of a urethane vinyl ether compound having a saturated urethane-containing polyester backbone and vinyl ether groups.

A first reaction vessel equipped with means for steam distillation and an nitrogen sparge was charged with 740 grams phthalic anhydride, 830 grams isophthalic acid, 1040 grams neopentyl glycol, 1060 grams diethylene glycol and 4.0 grams butyl stannoic acid catalyst. The charge was gradually heated to a temperature of 209° C. while a total of 605 milliliters of distillate containing water was removed. The resulting

product was a saturated polyester resin having an acid value of 1.1 milligrams of KOH/gram of sample.

This saturated polyester resin was then cooled to 36° C. at which time 368 grams of the divinyl ether of triethylene glycol was added thereto. The saturated polyester resin had a Gardner-Holdt bubble tube viscosity of $Z3^-$ at 25° C; a number-average molecular weight of 452 as determined by GPC using a polystyrene standard; and a measured hydroxyl value of 277.8 milligrams of KOH/gram of sample.

A second reaction vessel equipped with means for maintaining a blanket of nitrogen was charged at ambient temperature with 777 grams isophorone diisocyanate, 302.8 grams triethylene glycol divinyl ether, 11.0 grams triphenyl phosphite and 6.6 grams tetraphenyl dipropylene glycol diphosphite. The charge was heated under nitrogen to 105° C. over 30 minutes and held at that temperature for about 3 hours. The charge was then cooled to 60° C. over 1.25 hours. Thereafter, the vessel was allowed to cool to ambient temperature.

The charge was then heated under nitrogen to 34° C, and 0.2 grams dibutyl tin dilaurate was added thereto. Through an addition funnel, 706.8 grams of the saturated polyester resin prepared in this example were gradually added to the charge. The temperature was then gradually increases to 50° C. and held at that temperature for about 3.5 hours. Thereafter, the charge was heated to 70° C. at which time 405.5 grams of 4-hydroxy butyl vinyl ether were gradually added thereto.

The temperature was increased to 80° C. and held for 1 hour. The heat was then removed from the charge. The resulting product was a cocurable urethane vinyl ether compound which had a Gardner-Holdt bubble tube viscosity of S^- at 75 percent by weight solids in propylene glycol methyl ether. Infrared spectrum analysis showed that no residual isocyanato functionality remained therein.

EXAMPLE 3

Post-Reaction Treatment of the Urethane Vinyl Ether Compound with a Reducing Agent

This example illustrates the optional post-synthesis treatment of the urethane vinyl ether compound of Example 2 with reducing agent.

The saturated urethane vinyl ether compound from Example 2 was treated with a reducing agent. In this example, the reducing agent was added at the end of the reaction rather than in the second reaction vessel. Specifically, after the reaction was completed and infrared spectrum analysis confirmed that no isocyanato functionality remained in the resulting urethane vinyl ether, the charged vessel was heated to 70° C, at which time 11.0 grams triphenyl phosphite and 6.6 grams tetraphenyl dipropylene glycol diphosphite were added thereto. The charge was then gradually heated to 100° C. and held at that temperature for about 3 hours.

EXAMPLES 4 and 5

Preparation and Curing of Coating Compositions of the Present Invention

Examples 4 and 5 represent coating compositions prepared in accordance with the present invention. Example 4 represents a coating composition suitable for cure by ionizing radiation, and Example 5 represents a coating composition suitable for cure by actinic radiation.

The coating compositions of Examples 4 and 5 were prepared by mixing the ingredients set forth in TABLE 1. In TABLE 1, the triethylene glycol divinyl ether was blended with 0.3 weight percent triphenyl phosphite and 0.5 weight percent tetraphenyl dipropylene glycol diphosphite and, thereafter, held at room temperature for at least 16 hours prior to use. These weight percentages were based upon the weight of the triethylene glycol divinyl ether. Values in TABLE 1 represent percent by weight resin solids.

TABLE 1

Composition	Example 4	Example 5
Unsaturated polyester of Example 1	60.4	57.4
Urethane vinyl ether of Example 3	20.5	19.4
Triethylene glycol divinyl ether[1]	17.1	16.3
Flow modifiers[2]	2.0	1.9
Photoinitiator[3]	----	5.0

[1] RAPI-CURE® DVE-3 divinyl ether (triethylene glycol divinyl ether commercially available from ISP Corp.).
[2] 1.0 % 2-Methoxymethylethoxypropanol, commercially available as BYK-346 flow modifier from BYK Chemie; and 1.0 % organo silane, commercially as TEGO FLOW 425 flow modifier from Goldschmidt Chemicals.
[3] DAROCURE® 1173 photoinitiator (2-hydroxy-2-methyl-1-phenyl propane 1-one commercially available from Ciba-Geigy Corp.)

Each of four samples of the composition of Example 4 (herein designated Samples 4a, 4b, 4c, and 4d) and three samples of the composition of Example 5 (herein designated Samples 5a, 5b, and 5c) were drawn down on the backside of Penopac Form 1A paper substrate (commercially available from Leneta Co.) using a Pamarco handproofer draw-down bar with a 360 dots per inch (940 dots per centimeter) roller (commercially available from Pamarco Inc.) to provide wet films having a thickness of 0.09 mil (2.3 microns). The films were then cured and subjected to a mar test and a smudge test to determine their degree of cure.

The mar tests were performed by rubbing the cured film with a corner of a commercially-available wooden tongue depressor under the pressure generated merely from the weight of the hand holding the tongue depressor. If visible scratches were produced and remained, the film was considered to be marred. The number and severity of scratches determined the degree of mar. The full range of the cure scale with regard to the mar test is as follows:

Best Mar Results				Worst Mar Results
No mar	Very slight mar	Slight mar	Mar	Substantial mar

The smudge tests were performed by wiping the cured film with a smooth surface, such as the skin surface of a finger, under the pressure generated merely from the weight of the hand performing the smudge test. If visible indentations were made and remained, the film was considered to be smudged. The severity of the indentations determined the degree of smudge. Moreover, if, in addition to being smudged, coating physically transferred to the smooth surface performing the smudge test, the film was considered to be greasy. The full range of the cure scale with regard to smudge test is as follows:

Best Smudge Results					Worst Smudge Results
No smudge	Very slight smudge	Slight smudge	Smudge	Substantial smudge	Greasy

TABLE 2

SAMPLE	CURING CONDITIONS	REMARKS
4a	Electron beam (EB) in full nitrogen; at 1 megarad (MR); 200 kV, 5 mA, at 7.9 meters per minute (mpm).	No mar; no smudge.
4b	EB in full nitrogen; at 1 MR; 200 kV, 5 mA, at 22.2 mpm.	No mar; no smudge
4c	EB in 1500 ppm oxygen; at 3 MR; 200 kV, 5 mA, at 7.9 mpm.	No mar; no smudge
4d	EB in 3000 ppm oxygen; at 3 MR; 200 kV, 5 mA, at 7.9 mpm.	Slight mar; no smudge
5a	Ultraviolet light (UV) in air; 1 lamp, high power, (118 Watts/centimeter (cm)), at 30.5 mpm.	No mar; no smudge
5b	UV in air; 1 lamp, high power (118 Watts/cm), at 61.0 mpm.	No mar; no smudge
5c	UV in air; 1 lamp, high power (118 Watts/cm), at 91.5 mpm.	Substantial mar, smudge

The results set forth in TABLE 2 illustrate that radiation curable coating compositions prepared in accordance with this invention cure at relatively high line speeds, even when in the presence of oxygen.

EXAMPLE 6 , 7, 8 and 9

Radiation Curable coatings with an Optional Acrylate Component

Examples 6 through 9 represent coating compositions prepared in accordance with the present invention. Of these coating compositions, those prepared in Examples 6 and 7 include an optional acrylate component, and those prepared in Examples 8 and 9 did not include an optional acrylate component.

Examples 6, 7, 8 and 9 were prepared by mixing together the ingredients set forth in TABLE 3. In TABLE 3, the triethylene glycol divinyl ether was blended with 0.3 weight percent triphenyl phosphite and 0.5 weight percent tetraphenyl dipropylene glycol diphosphite and, thereafter, held at room temperature for at least 16 hours prior to use. These weight percentages were based upon the weight of the triethylene glycol divinyl ether. Values in TABLE 3 represent percent by weight resin solids.

TABLE 3

Composition	Example 6	Example 7	Example 8	Example 9
Unsaturated polyester of Example 1	49.3	49.9	58.6	61.6
Urethane vinyl ether of Example 3	11.7	11.5	13.9	14.6
Triethylene glycol divinyl ether[1]	19.0	19.4	22.7	23.8
Photoinitiator[2]	4.0	---	4.8	---
Epoxy diacrylate[3]	16.0	17.0	---	---
Viscosity @ 25° C. (centipoises)	---	800	---	2000

[1] RAPI-CURE DVE-3 divinyl ether, commercially available from ISP Corp.
[2] DAROCURE 1173 photoinitator, commercially available from Ciba-Geigy Corp.
[3] EBECRYL 3700 epoxy acrylate (the diester of a diglycidyl ether of bisphenol A commercially available from Radcure Specialties, Inc.)

Three samples of each of the compositions of Examples 6 and 8 (herein designated as Samples 6a, 6b, 6c, 8a, 8b and 8c) and four samples of each of the compositions of Examples 7 and 9 (herein designated as 7a, 7b, 7c, 7d, 9a, 9b, 9c and 9d) were drawn down using a 0.003 inch (0.08 millimeter) wirewound draw-down bar (commercially available from Paul N. Gardner Co.) on the back side of Penopac Form 1A paper substrate to give a wet film thickness of 0.15 mil (3.8 microns). The films were cured as set forth in TABLE 4. TABLE 4 also sets out level of cure observations as set out above.

TABLE 4

SAMPLE	CURING CONDITIONS	REMARKS
6a	UV in air, 1 lamp, high power; at 61.0 mpm	Slight mar; no smudge
6b	UV in air, 1 lamp, high power; at 76.2 mpm	Moderate mar; no smudge
6c	UV in air, 1 lamp, high power; at 91.5 mpm	Moderate mar; slight smudge
8a	UV in air, 1 lamp, high power; at 61.0 mpm	Slight mar; no smudge
8b	UV in air, 1 lamp, high power; at 76.2 mpm	Modreate mar; slight smudge
8c	UV in air, 1 lamp, high power; at 91.5 mpm	Modreate mar; slight smudge
7a	EB in 65 ppm oxygen; 1MR, 4.0 mA at 17.7 mpm	Very slight mar; no smudge
7b	EB in 50 ppm oxygen; 2 MR, 5.0 mA at 11.0 mpm	No mar, no smudge
7c	EB in 1000 ppm oxygen; 3 MR, 5.0 mA, at 7.3 mpm	No mar; no smudge
7d	EB in 2900 ppm oxygen; 3 MR, 5.0 mA, at 7.3 mpm	Moderate mar; no smudge
9a	EB in 65 ppm oxygen; 1MR, 4.0 mA at 17.7 mpm	Moderate mar, slight smudge
9b	EB in 50 ppm oxygen; 2 MR, 5.0 mA at 11.0 mpm	No mar; no smudge
9c	EB in 1000 ppm oxygen; 3 MR, 5.0 mA, at 7.3 mpm	No mar; no smudge

The results set forth in TABLE 4 illustrate that radiation curable coating compositions prepared in accordance with this invention, with the addition of an optional acrylate component, cure at relatively high line speeds, even when in the presence of oxygen.

EXAMPLES 10, 11, 12 and 13

Radiation Curable Coatings with and without a Urethane Vinyl Ether Compound

Examples 10 and 11 represent comparative coating compositions which do not contain a urethane vinyl ether compound, and Examples 12 and 13 represent coating compositions prepared in accordance with the present invention. A comparison of Examples 10 and 12 and a comparison of Examples 11 and 13 demonstrate the

improved cure response and oxygen tolerance during the curing process of radiation curable coating compositions prepared in accordance with the present invention.

The coating compositions of Examples 10, 11, 12 and 13, were prepared by mixing together the ingredients in TABLE 5. In TABLE 5, the triethylene glycol divinyl ether was blended with 0.3 weight percent triphenyl phosphite and 0.5 weight percent tetraphenyl dipropylene glycol diphosphite and, thereafter, held at room temperature for at least 16 hours prior to use. These weight percentages were based upon the weight of the triethylene glycol divinyl ether. Values in TABLE 5 represent percent by weight resin solids.

TABLE 5

Composition	Example 10	Example 11	Example 12	Example 13
Unsaturated polyester of Example 1	68.6	65.1	60.4	57.4
Urethane vinyl ether of Example 3	---	---	20.5	19.4
Triethylene glycol divinyl ether[1]	29.4	27.9	17.1	16.3
Photoinitiator[2]	---	5.0	---	5.0
Flow modifiers[3]	2.0	2.0	2.0	1.9

[1] RAPI-CURE®DVE-3 divinyl ether, commercially available from ISP Corp.
[2] DAROCURE® 1173 photoinitiator, commercially available from Ciba-Geigy Corp.
[3] 1.0 % 2-Methoxymethylethoxypropanol, commercially available under the trade designation BYK-346 flow modifier from BYK Chemie; and 1.0 % organo silane, commercially available under the trade designation TEGO FLOW 425 flow modifier from Goldschmidt Chemicals.

Samples of each composition of Example 10, 11, 12 and 13 were drawn down on the backside of Penopac Form 1A paper substrate using a Pamarco handproofer draw-down bar with a 360 dots per inch roller to provide wet films having a thickness of about 0.09 mil (2.3 microns). The films were cured as set forth in TABLE 6. TABLE 6 also sets out level of cure observations as set out above.

TABLE 6

Sample (UV Cure)	Run 1: 4.6 mpm; 79 Watts/cm; 3 lamps, full power	Run 2: 18.3 mpm; 79 Watts/cm; 1 lamp, full power	Run 3: 25.4 mpm; 79 Watts/cm; 1 lamp, full power
Example 11	No mar; no smudge	Substantial mar; smudge	Substantial mar; greasy
Example 13 (Invention)	No mar; no smudge	Slight mar; no smudge	Substantial mar; Very slight smudge
Sample (EB Cure)	Run 1: 3 MR; full nitrogen	Run 2: 3 MR; 800 ppm oxygen	Run 3: 3 MR; 1800 ppm oxygen
Example 10	No mar; no smudge	Mar; no smudge	Substantial mar; smudge
Example 12 (Invention)	No mar; no smudge	Mar; no smudge	Substantial mar; very slight smudge

The results set forth in TABLE 6 illustrate an improved cure rate at high line speeds under UV cure conditions and an improved oxygen tolerance under EB cure conditions exhibited by radiation curable coating compositions prepared in accordance with this invention.

EXAMPLES 14, 15, 16 and 17

Flexibility Testing of Radiation Curable Coating Compositions

These examples demonstrate the improved flexibility of radiation curable coating compositions prepared in accordance with the present invention. Specifically, Examples 14 and 16 represent comparative radiation curable coating compositions, and Examples 15 and 17 represent radiation curable coating compositions prepared in accordance with the present invention.

Coating compositions of Examples 14, 15, 16 and 17 were prepared by mixing together the ingredients set forth in TABLE 7. In TABLE 7, the triethylene glycol divinyl ether and the polytetrahydrofuran divinyl ether were separately blended with 0.3 weight percent triphenyl phosphite and 0.5 weight percent tetraphenyl dipropylene glycol diphosphite and, thereafter, held at room temperature for at least 16 hours prior to use. These weight percentages were based upon the weight of the divinyl ether to which they were added. Values in TABLE 7 represent percent by weight resin solids.

TABLE 7

Composition	Example 14	Example 15	Example 16	Example 17
Unsaturated polyester of Example 1	66.4	50.8	58.7	48.4
Urethane vinyl ether of Example 2	---	27.8	---	26.5
Triethylene glycol divinyl ether[1]	28.8	16.6	---	5.5
Polytetrahydrofuran divinyl ether[2]	---	---	36.5	14.8
(5) Photoinitiator[3]	4.8	4.8	4.8	4.8

[1] RAPI-CURE® DVE-3 divinyl ether, commercially available from ISP Corp.
[2] POLY-THF 290 divinyl ether commercially available from BASF Corp.
[3] DAROCURE® 1173 photoinitator, commercially available from Ciba-Geigy Corp.

A sample of each of the compositions of Examples 14, 15, 16 and 17 were drawn down on a pretreated aluminum panel (a chrome-pretreated aluminum alloy commercially available from Advance Coating Technology, Inc. as APR-19652) using a 0.018 inch (0.46 millimeter) wirewound draw bar and cured in ultraviolet light (2 lamps, 10.2 centimeters, 15.2 mpm, in air). All samples and the drawbar were heated to 120° F. (49° C.) prior to application.

Direct impact flexibility testing was performed using a GARDNER® impact tester with a 5/8 inch (1.6 centimeter) head as described in ASTM D2794. In accordance with these tests, if the direct impact resulted in visible cracking of the cured film, the result reported was "failed." The results of the direct impact tests are set forth in TABLE 8.

TABLE 8

SAMPLE	TEST LEVEL	RESULT
Example 14	15 inch-pounds	Failed
Example 15 (Invention)	15 inch-pounds	Passed
Example 16	20 inch-pounds	Failed
Example 17 (Invention)	20 inch-pounds	Passed

The results set forth in TABLE 8 illustrate the improved flexibility exhibited by radiation curable coating compositions prepared in accordance with the present invention.

EXAMPLES 18 AND 19

Preparation and Curing of Coating Compositions of the Present Invention for Determination of the Effect on Flexibility of the Urethane Vinyl Ether Compound

Examples 18 and 19 represent coating compositions prepared in accordance with the present invention. The coating compositions for Examples 18 and 19 were prepared by mixing the ingredients set forth in the following TABLE 9. The coating composition represented in Example 18 contains approximately 10% by weight solids of the urethane vinyl ether compound from Example 3, and the composition represented by Example 19 contains approximately 40% by weight solids of the urethane vinyl ether compound from Example 22. Values in TABLE 9 represent percent by weight by solids.

TABLE 9

COMPOSITION	EXAMPLE 18	EXAMPLE 19
Unsaturated polyester of Example 1	88.6	54.40
Urethane vinyl ether of Example 3	9.46	37.84
Triethylene glycol divinyl ether[1]	1.94	7.76

[1] RAPI-CURE®DVE-3 divinyl ether, commercially available from ISP Corp.

One sample of each of the coating compositions of Examples 18 and 19 (hereinafter designated as Sample 18a and 19a, respectively) was drawn down on aluminum substrate using a 0.018 inch (0.46 millimeters) wirewound draw bar. One sample of each of the coating compositions of Examples 18 and 19 (hereinafter designated as Samples 18b and 19b, respectively) was drawn down using a 0.032 inch (0.81 millimeters)wire wound draw bar. Each of the applied Samples 18a, 19a, 18b and 19b was cured by electron beam (EB curing conditions: 3 MR; 7.9 mpm; 5 mA; 35 ppm Oxygen). Testing of "free-films" was performed in accordance with ASTM D2370-92 using an INSTRON® Mini 44 Universal Mechanical Testing Apparatus. Each sample was divided into ten to twelve specimens. Thereafter, each specimen was subjected to the test parameters set forth in TABLE 10.

TABLE 10

SPECIMEN / TEST PARAMETER	VALUE
Test Mode	Tensile
Specimen Length	76.2 millimeters
Specimen Width	12.7 millimeters
Specimen Gauge Length (test length)	24.4 millimeters
Crosshead Speed	50 millimeters/minute
Data Sampling Rate	20 points/second

The average tensile properties of all free film specimens for the coating compositions represented by Examples 18 and 19 at the film thicknesses represented by Samples 18a, 18b, 19a and 19b are set forth in TABLE 11.

TABLE 11

Sample	Sample Description	Average Specimen Thickness (millimeters)	Average Young's Modulus (GPa)	Average Tensile Strength (MPa)	Average Breaking Strain (percent)
18a	10% urethane vinyl ether	0.025 ± 0.002	0.35 ± 0.02	10.2 ± 3.1	3.56 ± 1.39
19a	40% urethane vinyl ether	0.035 ± 0.001	0.19 ± 0.02	10.3 ± 0.5	9.84 ± 1.60
18b	10% urethane vinyl ether	0.043 ± 0.001	0.31 ± 0.01	6.4 ± 1.8	2.27 ± 0.82
19b	40% urethane vinyl ether	0.046 ± 0.001	0.20 ± 0.01	10.7 ± 0.9	9.21 ± 1.51

The results set forth in TABLE 11 illustrate that flexibility improves with the addition of increased levels of urethane vinyl ether in radiation curable coating compositions prepared in accordance with the present invention.

It is evident from the foregoing that various modifications, which are apparent to those skilled in the art, can be made to the embodiments of this invention without departing from the spirit or scope thereof. Having thus described the invention, it is claimed as follows.

We claim:

1. A radiation curable coating composition comprising:

(a) an unsaturated polyester compound,

(b) a polymerizable vinyl ether compound which is free-radically reactive with the unsaturated polyester compound, and which comprises at least one of the following:

(i) a compound having an average of greater than 1.0 reactive vinyl ether groups per molecule, and

(ii) a vinyl ether-containing group bonded to the unsaturated polyester compound such that there is an average of at least 1.0 reactive vinyl ether group per molecule; and

(c) a polymerizable urethane vinyl ether compound having a saturated, urethane-containing backbone with vinyl ether groups, wherein said urethane vinyl ether compound is free-radically reactive with the unsaturated polyester compound.

2. The composition of claim 1 wherein the ratio of carbon-carbon double bond equivalents of the sum of the vinyl ether groups from the vinyl ether compound and the urethane vinyl ether compound to carbon-carbon double bond equivalents from the unsaturated polyester compound ranges form about 0.1:1 to about 1.5:1.

3. The composition of claim 1 further comprising a photoinitiator.

4. The composition of claim 2 further comprising a thermal polymerization inhibitor.

5. The composition as recited in claim 2 wherein said unsaturated polyester compound comprises an unsaturated polyester polymer having a peak molecular weight, as measured by gel permeation chromatography using a polystyrene standard, ranging from about 500 to about 50,000.

6. The composition of claim 5 wherein the ratio of carbon-carbon double bond equivalents of the sum of the vinyl ether groups from the vinyl ether compound and the urethane vinyl ether compound to carbon-carbon double bond equivalents from the unsaturated polyester compound ranges form about 0.1:1 to about 1.4:1.

7. The composition as recited in claim 5 wherein said unsaturated polyester compound comprises an unsaturated polyester polymer having a peak molecular weight, as measured by gel permeation chromatography using a polystyrene standard, ranging from about 800 to about 25,000.

8. The composition as recited in claim 1 wherein the percentage of the carbon-carbon double bond equivalents of the sum of the vinyl ether groups from the vinyl ether compound and the urethane vinyl ether compound provided by the urethane vinyl ether compound ranges from about 1 percent to about 99 percent.

9. The composition of claim 1 wherein the composition consists essentially of the unsaturated polyester compound, the vinyl ether compound and the urethane vinyl ether compound.

10. The composition of claim 1 wherein the composition consists essentially of the unsaturated polyester compound, the vinyl ether compound, the urethane vinyl ether compound and a photoinitiator.

11. The composition of claim 1 wherein the composition consists essentially of the unsaturated polyester compound, the vinyl ether compound, the urethane vinyl ether compound and a thermal polymerization inhibitor.

12. The composition of claim 1 wherein the compositiou consists essentially of the unsaturated polyester compound, the vinyl ether compound, the urethane vinyl ether compound, a photoinitiator and a thermal polymerization inhibitor.

13. The composition of claim 1 wherein the unsaturated polyester compound comprises the reaction product of a polyhydric alcohol with an unsaturated carboxylic acid selected from the group consisting of maleic acid, fumaric acid and itaconic acid.

14. The composition of claim 13 wherein the unsaturated polyester compound includes a plurality of unsaturated polyester groups selected from the group consisting of: maleate groups, fumarate groups and itaconate groups.

15. The composition of claim 14 wherein unsaturated polyester compound includes a plurality of fumarate groups.

16. The composition of claim 1 wherein the urethane vinyl ether compound and the vinyl ether compound include a reaction product of a di-, tri-, or tetra-functional organic polyol and acetylene.

17. The composition of claim 1 wherein the vinyl ether compound comprises a compound selected from the group consisting of: tripropylene glycol divinyl ether, diethylene glycol divinyl ether, 1,4-butanediol divinyl ether, tetraethylene glycol divinyl ether, triethylene-glycol-divinyl ether, trimethylol propane trivinyl ether and polytetrahydrofuran divinyl ether.

18. The composition of claim 1 wherein the unsaturated polyester compound comprises a plurality of maleate groups, fumarate groups or both.

19. The composition of claim 1 wherein the unsaturated polyester compound comprises a plurality of fumarate groups.

20. A coated substrate comprising a substrate layer and a coating layer, wherein said coating layer comprises a cured coating composition, and wherein said coating composition comprises the radiation curable coating composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/21542

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L67/06 C08F283/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L C08F C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 01283 A (PPG INDUSTRIES INC) 18 January 1996 * see Examples E and 3 * see page 1, line 24-31; claims 1-26	1-20
X	EP 0 636 669 A (DSM NV) 1 February 1995 * see page 4, line 27 - page 5, line 32 * see page 2, line 49-51	1,3,5,7,9,10,20
Y	EP 0 322 808 A (PPG INDUSTRIES INC) 5 July 1989 cited in the application see page 2, line 37 - page 5, line 37	1-20
Y	WO 90 10660 A (DESOTO INC) 20 September 1990 see page 7, line 11-32	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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